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Novel adhesives comprising an elastomer composition comprising (1) at least 30 percent by weight of a triblock terpolymer elastomer having polystyrene end blocks and rubber poly(ethylene-butylene) midblocks; (2) at least 10 percent by weight of a diblock copolymer elastomer of styrene and ethylenebutylene; and (3) at least 30 percent by weight of non-liquid polyisobutylene, e.g. having a molecular weight of at least 800,000, or a copolymer containing at least 95% by weight of isobutylene; said adhesive composition further containing at least one tackifying resin in an amount sufficient to provide the desired balance of adhesive properties, e.g. tack; and adhesive tapes including same.

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54 **Adhesives.**

57 Novel adhesives comprising an elastomer composition comprising (1) at least 30 percent by weight of a triblock terpolymer elastomer having polystyrene end blocks and rubber poly(ethylene-butylene) midblocks; (2) at least 10 percent by weight of a diblock copolymer elastomer of styrene and ethylenebutylene; and (3) at least 30 percent by weight of non-liquid polyisobutylene, e.g. having a molecular weight of at least 800,000, or a copolymer containing at least 95% by weight of isobutylene; said adhesive composition further containing at least one tackifying resin in an amount sufficient to provide the desired balance of adhesive properties, e.g. tack; and adhesive tapes including same.

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ADHESIVES

The present invention is directed to adhesive compositions which may be characterised as possessing resistance to degradative environmental forces such as ultraviolet light (UV) and oxidation, are tacky to the feel, i.e. possess "perceived tack", have good shear resistance, are cost-efficient and can be processed into adhesive tapes by calendering as well as by other per se known coating means, e.g. solvent casting or extrusion coating.

Various adhesive compositions are known which possess some but not all of the above characteristics.

For example, so-called S-I-S adhesives having polystyrene end blocks and an isoprene midblock make excellent adhesives. However, due to the unsaturated isoprene midblock, they are not resistant to UV or oxidation. Accordingly, they are not useful for such applications as storm window tapes where they would be subjected to UV.

On the other hand, polyisobutylene adhesive formulations are essentially saturated and consequently are resistant to UV and oxidation. However, because they have minimal unsaturated hydrocarbon groups, they are not readily modified, e.g. by crosslinking, to provide acceptable shear resistance.

The acrylic family of adhesives combines the properties of resistance to shear, UV and oxidation. However, they are costly and cannot be made into adhesive tapes by calendering, a particularly efficacious coating means in the tape manufacturing art.

Relatively recently in the adhesive art, much attention has been focussed on a class of adhesives designated as S-EB-S which are thermoplastic rubbers having polystyrene end blocks and rubbery ethylene-butylene midblocks. The ethylene-butylene midblocks are regarded in the rubber industry as being saturated due to the presence of minimal unsaturated hydrocarbon groups. Consequently, the S-EB-S elastomers should in theory obviate the above-noted problem of the unsaturated isoprene midblock in S-I-S adhesives and provide an adhesive having the requisite UV and oxygen stability. However, as will be detailed more particularly hereinafter, they are not tacky and attempts to incorporate the usual tackifiers, i.e. those which are cost-effective and consequently commonly employed in the adhesive art, failed to provide an adhesive which possesses perceived tack or has tack measurable by conventional instrumentation, e.g. the Polyken (trademark of The Kendall Company) probe tack instrument.

Having failed to obtain an S-EB-S adhesive having the requisite tack, Applicants then theorized that what was needed was an elastomeric component having a shorter chain. Based upon this assumption, they then blended the diblock copolymer, polystyrene-poly(ethylene-butylene) (S-EB) with S-EB-S in various amounts ranging from 20-75% S-EB along with equivalent amounts of tackifier. While the resulting composition was slightly better in terms of perceived tack, there was still no measurable tack.

The task of the present invention in essence can be said to be to solve the aforementioned problems and thus provide an adhesive formulation which, as mentioned above, has the requisite stability against UV and oxidation, possesses the desired adhesive proper ties of acceptable levels of tack and resistance to shear, is cost-efficient, and can be applied to a suitable backing material to form an adhesive tape by calendering as well as by the other known coating means such as solvent casting or extrusion.

In accordance with the present invention, there is provided an elastomer composition comprising: (1) at least 30 percent of a triblock terpolymer elastomer having polystyrene end blocks and rubbery poly-(ethylene-butylene) midblocks; (2) at least 10 percent of a diblock copolymer elastomer of styrene and ethylene-butylene; and (3) at least 30 percent of non-liquid polyisobutylene, e.g. having a number average molecular weight of at least 800,000, or a copolymer containing at least 95% by weight of isobutylene (all percentages being by weight); the composition further containing (4) at least one tackifying resin in an amount sufficient to provide the desired adhesive properties.

Liquid polyisobutylenes are unsatisfactory because they act as plasticisers rather than imparting finger tack to the composition as is the case when solid polyisobutylene or the said solid copolymers thereof are used.

These adhesive formulations may be coated onto any of the per se known backing materials for adhesive tapes by calendering or other coating techniques. By electing the appropriate backing material and tailoring the ratios of ingredients to the particular desired end use, a whole line of adhesive tapes may be provided utilizing the novel adhesive formulations of this invention.

As was discussed above, attempts to blend a standard tackifying resin with the S-EB-S elastomer alone or in combination with the S-EB diblock elastomer failed to provide a rubber mix possessing measurable tack.

As examples of the conventional tackifying resins so tested, mention may be made of "Piccolyte" S-85;

"Foral" 105; "Polypale"; "Staybellite" ester 10; and "Regalrez" 1018 and 1078 (trademarks of Hercules Chemical); "Nirez" M105, 1085, 1100, and M-85; "Statac" B; "Super Statac" 80 and 100 (trademarks of Reichold Chemical); "Escorez" 1315 and 5380 (trademark of Exxon); "oulutac" 70 (trademark of Oulu); "super Ester" 18 (trademark of Arakawa); "Zonester" 85; and "Zonarez" B-115 and M-115 (trademarks of Arizona Chemical).

It has been discovered, quite unexpectedly, however, that the desired tack may be achieved along with the aforementioned other requisite properties (stability to UV and oxidation, shear resistance, cost and ability to coat by calendaring or other per se known coating techniques) by blending the tackifier with a rubber mix comprising:

- (1) at least 30 percent S-EB-S;
- (2) at least 10 percent of S-EB; and
- (3) at least 30 percent of non-liquid polyisobutylene (PIB), as previously described.

By way of illustration, the three-component rubber mix may comprise the following percentages of the three elastomers:

S-EB-S	30-40%
S-EB	10-40%
PIB	30-55%

A particularly preferred blend comprises a 40-20-40 blend of the respective components.

The tackifiers which may be employed are those which are understood in the art to possess minimal unsaturated hydrocarbon groups and are accordingly characterised as being tackifying resins which are stable against the degradative forces of UV and oxidation. Suitable resins of this functional description will be readily apparent to those skilled in the art. However, by way of illustration, mention may be made of saturated hydrocarbon, beta-terpene, hydrocarbon ester and pinene tackifying resins.

The amount of resin to be incorporated may vary over a wide range in accordance with the desired degree or balance of adhesive properties which is contemplated.

With respect to the amounts of various additives which may be incorporated in a rubber mix, it is standard terminology to recite the quantity as "phr", i.e. parts per hundred by weight of the rubber mix. Accordingly, and by way of illustration, useful adhesives in accordance with the practice of this invention have been prepared employing from about 80 to about 150 phr of resin, i.e. from 80-150 parts by weight of resin for each 100 parts by weight of rubber components.

In addition to the tackifying resin, the adhesive mix may contain other reagents performing specific desired functions, for example plasticizers, fillers, extenders, colourants such as titanium dioxide or carbon black, etc.

The novel adhesive formulations of this invention may be prepared by methods per se known in the rubber adhesive art and the manner or method of preparation per se accordingly comprises no part of this invention.

On a laboratory scale, the adhesives described in the illustrative examples given herein were prepared by mixing the three elastomers and a portion of the tackifier (e.g. of the order of 50 phr of tackifier) on a two-roll rubber mill, and then adding the remaining tackifier and other reagents along with sufficient organic solvent to dissolve the materials to provide an adhesive formulation having sufficient fluidity for coating, e.g. of the order of 70% solids. Suitable organic solvents for this purpose, e.g. toluene, heptane/toluene blends, hexane, etc. will be readily apparent to those skilled in the art.

While this method of preparation is entirely satisfactory on a laboratory scale, it is envisioned that for commercial production runs, the initial premix of elastomers and a portion of the tackifier will be done in an internal mixer such as a Banbury mixer. The remaining ingredients may then be incorporated in the resulting mix, e.g. the Banbury mix, in a manner known in the art utilizing such equipment as a twin screw extruder or a two-roll mill. A preferred method, however, comprises the use of cavity transfer mixer such as is disclosed in U.S.P. 4,419,014 in accordance with the procedures described and claimed in U.S.P. 4,687,794 issued to Huddleston or the copending British Patent Application No. 8710169, Serial No. 2195093.

The triblock S-EB-S elastomers which may be employed in the practice of this invention include those of the "Kraton G" series (trademark of Shell Chemical Company). Illustrative examples of these thermoplastic rubbers with their styrene/rubber ratios shown in parenthesis are: G-1650 (28/72); G-1651 (33/67); G-1652 (29/71); G-1657 (14/86); and G-4609 (33/67).

Since the S-EB diblock component is not readily commercially available, a particularly useful method of incorporating this component is by utilization of Kraton G 1726 (Shell Chemical) which comprises 70% S-EB and 30% S-EB-S. Accordingly, it is to be understood that when employing Kraton G 1726, a portion of the triblock S-EB-S will be provided in this manner, with the remainder being incorporated with S-EB-S alone, e.g. one of the aforementioned triblocks of the Kraton G series.

To illustrate, a 40/20/40 ratio of S-EB-S, S-EB and PIB may be obtained by admixing the following:

Kraton G 1652	63 gms
Kraton G 1726	57 gms
PIB	80 gms

[As will be apparent from the foregoing discussion, the 57 grams of Kraton G 1726 comprises approximately 40 grams of S-EB and 17 grams of S-EB-S. This 17 grams plus the 63 grams of Kraton G 1652 will provide the 80 grams of S-EB-S.]

The following examples show by way of illustration and not by way of limitation the practice of this invention.

EXAMPLE 1

A rubber premix was prepared by mixing the following proportions by weight of ingredients on a two-roll mill:

Kraton G 1652	63
Kraton G 1726	57
Vistanex L-80 (trademark of Exxon for a PIB elastomer)	80
Piccolyte S-85 (trademark of Hercules for a betaterpene resin)	100
Titanium Dioxide (white pigment)	20
	<u>320</u>

Vistanex L-80 is a solid polyisobutylene having a number average molecular weight of 900,000.

The resulting mix contains 62% of the three-elastomer blend, the remaining 38% being the resin (50 phr) and titania (10 phr). Accordingly, 100 grams of this formulation will contain:

S-EB-S (Kraton G 1652)	25.0 gms
S-EB (Kraton G 1726)	12.5 gms
PIB (Vistanex)	25.0 gms
Beta-terpene Resin (Piccolyte S-85)	31.0 gms
TiO ₂	6.5 gms
	<u>100.0 gms</u>

To 100 gms of this mix were added, with mixing, an additional 31.0 gms (50.0 phr) of Piccolyte S-85 resin making a total of 100.0 phr), 31 gms (50 phr) of "super Statac" 80 (trademark of Reichhold for a saturated hydrocarbon resin); and 12.5 gms (20 phr) of a plasticizing oil, "Shelliflex" 371 (trademark of Shell Chemical) dissolved in sufficient toluene to provide an adhesive formulation having approximately 70% solids content, identified hereinafter as Formula 1.

EXAMPLES 2 to 15

Example 1 was repeated, varying the resins and their amounts to provide formulations 2-15, respectively, as set forth in Table 1.

EXAMPLES 16 to 21

Example 1 was repeated, varying the amounts of plasticizer to provide formulations 16-21, respectively,
 5 as set forth in Table 1.

EXAMPLES 22 to 26

10 Example 1 was repeated varying the amounts of the diblock and triblock elastomers to provide
 formulations 22-26, respectively, as set forth in Table 1.

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	<u>TABLE 1A</u>								
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>
S-EB-S ¹	40	40	40	40	40	40	40	40	40
Elastomer (phr)									
20 S-EB ²	20	20	20	20	20	20	20	20	20
Elastomer (phr)									
PIS ³	40	83	40	40	40	40	40	40	40
25 Elastomer (phr)									
S-85 ⁴	100	83	67	125	100	50	50	85	54
Resin (phr)									
30 SS 80 ⁵	50	42	20					40	26
Resin (phr)									
Z 85 ⁶							50		
Resin (phr)									
35 SE 10 ⁷						50			
Resin (phr)									
Shellflex	20	20	20	20	20	20	21	20	20
40 Plasticizer (phr)									
TiO ₂	10	10	10	10	10	10	10	10	10
Pigment (phr)									

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TABLE 1B

		<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>
5	S-EB-S ¹	40	40	40	40	40	40	40	40	40
	Elastomer (phr)									
	S-EB ²	20	20	20	20	20	20	29	20	20
	Elastomer (phr)									
10	PIS ³	40	40	40	40	40	40	40	40	40
	Elastomer (phr)									
	S-85 ⁴	68	75	72	95	102	61	85	85	85
15	Resin (phr)									
	SS 80 ⁵	32	35	38	45	48	29	40	40	40
	Resin (phr)									

TABLE 1B (continued)

		<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>
25	Z 85 ⁶									
	Resin (phr)									
	SE 10 ⁷									
30	Resin (phr)									
	Shellflex	20	20	20	20	20	20	5	10	15
	Plasticizer (phr)									
	TiO ₂	10	10	10	10	10	10	10	10	10
35	Pigment (phr)									

TABLE 1C

		19	20	21	22	23	24	25	26
5	S-EB-S ¹	40	40	40	30	35	40	45	50
	Elastomer (phr)								
	S-EB ²	20	20	20	30	25	20	15	10
	Elastomer (phr)								
10	PIS ³	40	40	40	40	40	40	40	40
	Elastomer (phr)								
	S-85 ⁴	85	85	85	85	85	85	85	85
15	Resin (phr)								
	SS 80 ⁵	40	40	40	40	40	40	40	40
	Resin (phr)								
20	Z 85 ⁶								
	Resin (phr)								
	SE 10 ⁷								
	Resin (phr)								
25	Shellflex	20	25	30	20	20	20	20	20
	Plasticizer (phr)								
	TiO ₂	10	10	10	20	20	20	20	20
30	Pigment (phr)								

35 Notes on Tables 1A, 1B and 1C

1. Kraton G 1652 & Kraton G 1726
2. Kraton G 1726
- 40 3. Vistanex L-80
4. Piccolyte 5-85
5. Super Statac 80
6. "Zonester" 85 (Arizona)
7. Stabellite Ester 10 (Hercules)

45 The adhesive formulations prepared in the foregoing illustrative examples were calendered onto a polyethylene backing at a thickness of the order of 2.0 mils (± 0.2) and the resulting adhesive tapes were then subjected to the standard adhesive tests recited in Tables 2A and 2B.

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TABLE 2A

	<u>Formula</u>	Adhesion ¹	Adhesion ¹	Probe ²
		Steel	Polyethylene	Tack
		<u>oz/inch width</u>	<u>oz/inch width</u>	<u>gm/cm²</u>
5	1	84		294
	2	52		297
10	3	44		417
	4	60		292
	5	56		367
15	6	48		542
	7	47		497
	8	49	27	315
	9	40	18	150
20	10	39	20	330
	11	48	23	311
	12	46	28	322
25	13	66	30	261
	14	40	22	243

TABLE 2A (continued)

	<u>Formula</u>	Adhesion ¹	Adhesion ¹	Probe ²
		Steel	Polyethylene	Tack
		<u>0.2/inch width</u>	<u>0.2/inch width</u>	<u>gm/cm²</u>
35	15	40	17	111
	16	53	9	15
40	17	48	20	78
	18	40	24	249
	19	42	22	441
	20	23	28	350
45	21	26	17	448
	22	42	24	404
	23	58	29	104
50	24	44	22	380
	25	54	26	271
	26	48	25	487

TABLE 2B

		Loop	Hold Power ³	Hold Power ³
		Tack	at 100°F (°C)	at 120°F (°C)
5	<u>Formula</u>	ozs/inch	<u>for hours</u>	<u>for hours</u>
		<u>width</u>		
	1		> 100 hrs.	
10	2		"	
	3		"	
	4		"	
15	5		"	
	6		"	
	7		"	
20	8	14		> 48 hr
	9	3		47
	10	8		> 48
	11	16		> 48
25	12	8		> 48

TABLE 2B (continued)

30	13	12		8.7
	14	8		42
	15	8		> 48
35	16	0		
	17	2		> 48
	18	4		> 48
40	19	10		> 48
	20	14		> 48
	21	21		6
45	22	8		11
	23	9		> 48
	24	6		> 48
	25	10		> 48
50	26	9		> 48

55 Notes on test methods used in Tables 2A and 2B.

1. Adhesion - 180° Peel - ASTM D-1000.

2. Probe Tack - ASTM E-171.

3. Hold power 1 square inch with 1 Kilogram weight, ASTM D3654.

In addition to the above adhesive tests, the novel adhesive compositions of this invention were subjected to UV and oxidation stability testing by subjecting them to four months direct contact to summer sunshine, facing the sky at a 45° angle to the ground, southern exposure. No visual degradation was observed and the adhesive was functional, peeled cleanly and was tacky. As distinguished therefrom, the prior rubber-based adhesives, when subjected to the same test conditions will, as a class lose their adhesive properties and become a "gooey" mess within 72 hours.

Since certain changes may be made without departing from the scope of the invention herein described, it is intended that all matter contained in the foregoing description, including the examples, shall be taken as illustrative and not in a limiting sense.

15 Claims

1. An adhesive composition including an elastomer composition containing S-EB-S adhesive characterised in that the elastomer composition comprises:

- (1) at least 30 percent by weight of a triblock terpolymer elastomer having polystyrene end blocks and rubbery poly(ethylene-butylene) midblocks;
- (2) at least 10 percent by weight of a diblock copolymer elastomer of styrene and ethylene-butylene; and
- (3) at least 30 percent by weight of a non-liquid polyisobutylene or a copolymer containing at least 95 percent by weight of isobutylene; the said adhesive composition further including at least one tackifying resin.

2. A composition as claimed in Claim 1 in which the polyisobutylene or the copolymer have a number average molecular weight of at least 800,000.

3. An adhesive composition as claimed in Claim 1 or Claim 2 characterised in that the said resin possesses minimal unsaturated hydrocarbon groups and is characterised as being a tackifying resin which is characterised as being stable against the degradative forces of ultraviolet radiation and oxidation.

4. An adhesive composition as claimed in Claim 1, 2 or 3 characterised in that the said resin is a saturated hydrocarbon, beta-terpene, hydrocarbon ester or pinene tackifying resin or a mixture thereof.

5. An adhesive composition as claimed in any one of Claims 1 to 4 characterised in that the amount of resin is from about 80 to about 150 parts per hundred.

6. An adhesive composition as claimed in any one of Claims 1 to 5 characterised in that the said triblock terpolymer elastomer contains a styrene/ethylene-butylene ratio of from 14/86 to 33/67.

7. An adhesive composition as claimed in any one of Claims 1 to 6 characterised in that the said elastomer composition comprises from about 30 to about 40 percent by weight of said triblock terpolymer; from about 10 to about 40 percent by weight of said diblock copolymer; and from about 30 to about 55 percent of said isobutylene polymer.

8. An adhesive tape comprising a support layer carrying, on one side thereof, an adhesive composition as claimed in any one of Claims 1 to 7.

9. An adhesive tape characterised as possessing resistance to degradative environmental forces of ultraviolet light and oxidation, as being tacky to the feel, as having good shear resistance, and as being cost-effective, the said tape comprising a support carrying on one surface thereof a layer of adhesive including an elastomer composition comprising:

- (1) at least 30 percent by weight of a triblock terpolymer elastomer having polystyrene end blocks and rubbery poly(ethylene-butylene) midblocks;
- (2) at least 10 percent by weight of a diblock copolymer elastomer of styrene and ethylene-butylene; and
- (3) at least 30 percent by weight of a non-liquid polyisobutylene or a copolymer containing at least 95 percent by weight of isobutylene; said adhesive composition further including at least one tackifying resin; said adhesive layer further including at least one tackifying resin, any said tackifying resin in said layer possessing stability against ultraviolet radiation and oxidation.

10. An adhesive tape as claimed in Claim 8 or Claim 9 characterised in that the said support layer comprises polyethylene.

11. A method of preparing an adhesive tape characterised in that it comprises the step of calendering onto a support layer an adhesive composition as claimed in any one of Claims 1 to 7.

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